

A Theoretical Study on the Effect of Lanthanide Ion Doping on the Excited State Properties of Yttrium Oxide and Yttrium Oxy-Sulphide

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【Introduction】

Recently, lanthanide ion doped yttrium oxide compounds have been attracting attention in applications concerning opto-electronic materials such as optical wave-guide films. Consequently study of the excited state of lanthanide ion doped yttrium oxide is of major significance. In the present work we report studies performed on the electronic excited states of europium ion doped yttrium oxide as well as yttrium oxy-sulphide using time-dependent density functional theory (TDDFT) method oriented to unveil the influence of lanthanide ion in yttrium oxide compounds.

【Method】

Electronic structure calculations for different spin multiplicities of Y_2O_3 and Y_2O_2S and its Eu doped analogues have been performed using DFT method employing DMol³ program embedded in the Materials Studio package. The functional used through out this study is the Becke non-local hybrid exchange functional and the non-local Lee-Yang-Parr 1988 correlation functional (BLYP) at the generalized gradient approximation (GGA) level. DNP (Double Numerical with Polarization) basis set and ECP (Effective Core Potential) were employed. The lowest excitation energies of spin-allowed and spin-forbidden transitions for the cluster models were calculated within TDDFT formalism as implemented in Gaussian03 program. Stuttgart/Dresden ECP's (SDD) basis set was used for the excited state calculations.

【Results and Discussion】

The calculated energy gap between the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of Y_2O_3 crystal is 4.4 eV, which is ~1.2 eV less than experimental band gap of 5.6 eV, which is a common drawback of the DFT method. The HOMO is mainly composed of O 2p orbitals and the LUMO is mainly composed of Y 4d orbitals. The calculated Y-O bond length is 2.29 Å, which agrees exactly with the experimental bond length 2.29 Å obtained by X-ray diffraction and EXAFS measurements. The calculated binding energy for different spin multiplicity of undoped and Eu doped Y_4O_6 and $Y_4O_4S_2$ clusters is shown in Fig. 1. We can observe that the singlet states of Y_4O_6 and $Y_4O_4S_2$ are the most stable. This indicates that the ground states of Y_4O_6 and $Y_4O_4S_2$ have singlet multiplicities. In the case of their Eu doped analogues, septet states are stable and next high lying states are quintet. This indicates that in absorption/emission spectroscopy the transition between septet and quintet state could be observed, which agrees with experiment, where the emission is from $^5D_0 \rightarrow ^7F_j$. The excitation spectrum of Y_4O_6 cluster shows wide absorption bands in the range between 267 to 385 nm, containing two broad bands located at 301 nm and 376 nm. These two broad bands are due to charge transfer from O 2p orbital to Y 5s orbital and small contribution to Y 4d orbital. The excitation spectrum of $Y_4O_4S_2$ cluster also shows a wide absorption band ranging from 288 to 360 nm, containing two broad bands located at 301 nm and 359 nm. These bands can be attributed to the charge transfer from O 2p and S 3p to Y 4d orbitals. After introducing one Eu dopant ion in the cluster model, there is a significant change in the excitation spectrum. The Eu doped Y_4O_6 cluster shows absorption bands ranging from 270 to 483 nm containing two broad bands at 301 and 369 nm and two narrow peaks at 396 and 464 nm. These two broad bands can be attributed to the charge transfer between cation Eu^{3+} and anions in the cluster. Two narrow peaks are due to f-f transition of Eu^{3+} ion, which is in good agreement with experimental result. Similar result is obtained for Eu doped $Y_4O_4S_2$ cluster having absorption bands in the range 290 to 467 nm containing two broad bands and two sharp peaks. The two broad bands located at 301 and 358 nm are due to charge transfer from O 2p and S 3p to Eu 5d orbital. The two sharp peaks beyond 430 nm are due to f-f transition of Eu^{3+} cation. Eu doped Y_4O_6 and $Y_4O_4S_2$ shows absorption bands shifted towards higher wavelength region and the additional narrow peaks are absent in the undoped clusters.

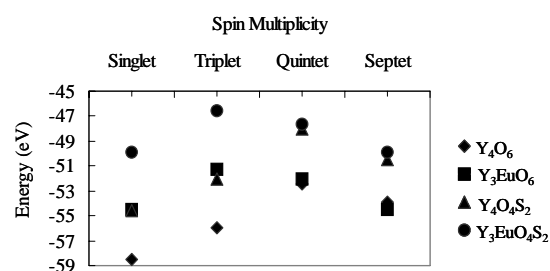


Fig. 1 Energy diagram for different spin multiplicities of undoped and Eu doped Y_4O_6 and $Y_4O_4S_2$ clusters.